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Macro-Ion Emission Study From Pyrolysis Products Of Carbon-Containing Wastes After Ashing.

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ABSTRACT

In this paper, they studied the emission of anions and cations from a potential sorption material obtained by pyrolysis from rubber waste and treated with "dry" ashing. The use of a solid pyrolysis product after ashing involves the purification of waste water from contaminants. The content of macro-ions in the aqueous extract of pyrolysis solid product from rubber waste was determined by ion chromatography. In order of mass concentration value decrease, macro-ions are located in the following series: SO_4^{2-}, Ca^{2+}, K^+, Na^+, Cl^-, Mg^{2+}, NH_4^+, NO^{3-}, F^-. A priority series in order of numerical value decrease concerning the coefficient K_{ww} in relation to wastewater: SO_4^{2-}, Na^+, NH_4^+, Cl^-, NO^{3-}. The obtained results show that the aqueous extract of the studied solid pyrolysis product from carbon-containing waste products after treatment with "dry" ashing does not exceed the normative indices for sewage by macro-ion content. They studied the toxicity of the pyrolysis product by biotesting according to the methot of water extract toxicity determination from soils, sewage sludge and waste, drinking water, sewage and natural water by the mortality of Daphni amagna Straus test object. They determined the hazard class of the pyrolysis product from the shredded wastes of used automobile tires after treatment. They established that the solid pyrolysis product from carbonaceous wastes after its treatment with ashing does not pollute wastewater, which justifies the possibility of its use from environmental positions with the restriction of wash water discharge into fishery water reservoirs.

Keywords: pyrolysis, adsorption, carbon-containing waste, emission, macro-ions.

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INTRODUCTION

Currently, an urgent task is to protect the environment from pollutants entering it. In the conditions of urban agglomeration, household and production activity of a person generate liquid wastes in the form of sewage, which are discharged into the sewage system. The cleaning of domestic and industrial wastewater is an urgent task for urbanized areas [1].

Mechanical, chemical, physical-chemical and biological methods are used for sewage treatment. Most of them are energy intensive, complex in technological execution and are oriented to expensive reagents [2]. Activated carbon, zeolites, natural materials, etc. are used most often as sorbents. For the most part, the sorption materials used are of high cost and require the use of natural resources.

At the same time, Russia has accumulated a variety of waste that can be processed into useful products, for example, in sorbents [3]. At the same time there is no need to develop mining or grow new raw materials, which inevitably leads to new pollution of the environment.

Carbonaceous waste contains organic components and often minerals, which are converted to gaseous pyrolysis fuel, liquid pyrolysis fuel and solid pyrolysis product during pyrolysis. A solid pyrolysis product formed at high temperature is a potential sorbent, the sorption properties of which can be improved by a special procedure - "dry" ashing [4].

In order to create highly effective sorption materials, it is necessary to carry out a qualitative and a quantitative analysis that will allow to determine the mass content of constituents in mobile and water-soluble forms.

METHODS

They studied the aqueous extract of the pyrolysis product from rubber waste after its treatment with ashing to determine the volumes of harmful substance emission by ion chromatography using the chromatograph "Stayer" [5].

To prepare an aqueous extract of the pyrolysis product from rubber waste, they dissolved 30 g of the sample in 150 ml of distilled water. The resulting suspension was treated for 30 minutes in a laboratory shaker, settled and filtered [6,7].

"ANION 4100" ion meter was used to measure the pH of the solutions. The mineralization and the specific electric conductivity were measured with "ANION-7020" conductometer [8].

The toxicity study of the solid pyrolysis product from carbon-containing wastes by biotesting was performed according to the method [9] of toxicity determination by the mortality of the test object Daphnia magna Straus.

RESULTS AND DISCUSSION

The sample of the pyrolysis product from carbon-containing waste produced by low-temperature pyrolysis under production conditions was taken as a research object. Waste rubber (tires) was subjected to pyrolysis processing. Subsequently, the resulting solid pyrolysis product of rubber waste was treated by ashing in a muffle furnace at t = 800 °C and examined for the emission of harmful elements from the obtained sample.

The solid pyrolysis product of waste rubber treated with "dry" ashing is the powder of gray color without foreign inclusions (Fig. 1).

Figure 1: Solid pyrolysis product after ashing

pH, mineralization, specific electrical conductivity, and macro-ion content were determined in the aqueous extract of the test sample. The results of measurements and normative indices for water bodies are given in Tables 1-2. For comparison, the tables demonstrate the maximum permissible concentration of the ingredient in the drinking water ($TLV_{drinking\ water}$), the maximum permissible concentration of the ingredient in the water of fishery reservoirs ($TLV_{open\ reservoirs}$), the permissible concentration of pollutants in the wastewater admitted for discharge to the centralized water disposal system ($LV_{wastewater}$) [10].

Table 1: Indices of aqueous extract of solid pyrolysis product after ashing

sample	pH, units pH	SEC, µS / cm	mineralization by NaCl, mg / dm^3	mineralization by the sum of macro-ions, mg / dm^3
rubber waste	6.9	785	382	404
$TLV_{drinking\ water}$	6.0-9.0	-	1000	1000
$TLV_{open\ reservoirs}$	6.5-8.5	-	1000	1000
$LV_{waste\ water}$	6.0-9.0	-	3000	3000

According to the obtained results, the mineralization of the water extract from the solid pyrolysis product after the treatment with ashing does not exceed the comparable standards for drinking water, fishery water and wastewater. A relatively high value of mineralization indicates a greater emission of macro-ions into the aqueous phase, which is confirmed after an experimental determination of macro-ion content (Table 2).

The pH value of 6.89 indicates an almost neutral aqueous extract medium of the treated solid pyrolysis product. Neutral value means that the sample is not contaminated with acids and alkalis. The use of the pyrolysis product as a sorption material will not lead to pH change, and hence the excess of this norm for drinking-water and cultural-utility water bodies, fishery reservoirs and sewage.

Table 2: Macro-ions of aqueous extract of solid pyrolysis product after ashing

sample		concentration, mg / dm^3								
	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
rubber waste	2.8	20.8	51.8	7.7	89.2	0.16	15.5	0.72	-	215
$TLV_{drinking\ water}$	2	200	-	50	-	1.5	350	45	3.5	500
$TLV_{open\ reservoirs}$	0.5	120	50	40	180	0.1	300	40	0.05 (for P)	100
$LV_{waste\ water}$	50	200	-	-	-	-	1000	50	12(for P)	1000

According to the results of chromatographic studies, the macro-ions subjected to emissions into the aqueous phase are arranged in the following order of value decrease (Table 3):

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Table 3: Ranks of priority of macro-ions in aqueous extract

rubber waste	SO_4^{2-}, Ca^{2+},K^+,Na^+,Cl^-,Mg^{2+},NH_4^+, NO^{3-}, F^-

In order to assess the degree of the studied pyrolysis product contamination after ashing against water bodies, they use the comparison with the normative indicators for drinking water, fishery water, sewage for discharge to a centralized system. Concentration factors were calculated with respect to $TLV_{drinking\ water}$, $TLV_{open\ reservoirs}$, $LV_{wastewater}$ according to the following formulas:

the concentration coefficient relative to the TLV of the macro-ion in the water of drinking, domestic and cultural objects.

$$K_{drinking\ water} = \frac{C}{TLV_{drinking\ water}} \quad (1)$$

б) the concentration coefficient relative to TLV of the macro-ion in the waters of fishery reservoirs.

$$K_{open\ reservoirs} = \frac{C}{TLV_{open\ reservoirs}} \quad (2)$$

в) the concentration coefficient relative to the permissible concentration of pollutants in the waste water admitted for discharge to the centralized water disposal system.

$$K_{waste\ water} = \frac{C}{LV_{waste\ water}} \quad (3)$$

The results are shown in Table 4.

Table 4: Coefficient of concentration of macro-ions aqueous extract relative TLV

Index	rubber waste		
	K_{dw}	K_{or}	K_{ww}
mineralization by NaCl	0.38	0.38	0.13
NH_4^+	1.40	5.58	0.06
Na^+	0.10	0.17	0.10
K^+	-	1.04	-
Mg^{2+}	0.15	0.19	-
Ca^{2+}	-	0.50	-
F^-	0.11	3.16	-
Cl^-	0.04	0.05	0.02
NO_3^-	0.02	0.02	0.01
PO_4^{3-}	-	-	-
SO_4^{2-}	0.43	2.15	0.72
mineralization by the sum of macro-ions	0.40	0.40	0.13

The use of a solid pyrolysis product from rubber waste after the treatment with "dry" ashing assumes the purification of waste water from pollutants. The obtained results show that the aqueous extract of the test sample does not exceed the normative parameters for water objects by the content of macro-ions.

The comparison by the concentration coefficient with respect to the permissible concentration of pollutants in wastewater admitted for discharge to a centralized water disposal system (Table 4) is illustrated by the diagram (Figure 2). The diagram is conveniently presented on a logarithmic scale according to the base 10.

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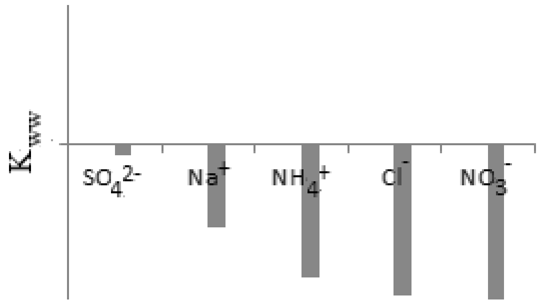

Figure 2: Coefficient of concentration of ingredients of aqueous extract of solid pyrolysis product after ashing relative to TLVforwaste water in base 10 logarithmic scale.

On the diagram, the macro-ions of which in the aqueous extraction of the solid pyrolysis product after treatment with ashing exceed the permissible concentration of pollutants in the wastewater admitted for discharge to the centralized water drainage system ($LV_{waste\ water}$), are located above the horizontal line, and the macro-ions with the volume less than the normative indicator are located lower.

Thus, in order of concentration coefficient decrease relative to the permissible concentration of pollutants in the wastewater admitted for discharge to the centralized water disposal system (K_{ww}) the macro-ions are arranged in the following row (Table 5):

Table5: Ranks of priority of macro-ions in aqueous extractas reduction of danger to waste water

rubber waste	SO_4^{2-},Na^+, NH_4^+,Cl^-,NO^{3-}

The absence of normative indices exceeding in water objects for macro-ions should indicate a low toxicity of the pyrolysis product being studied. The use of it as a sorption material is also limited by the possible toxicity. Therefore, there is a need to determine the toxicity of SPP after ashing experimentally by the mortality of Daphnia magna Straus test object. The results of the study are shown in Table 6.

Table 6: Toxicity of of solid pyrolysis product after ashing

sample	$BKR_{10\text{-}48}$	hazard class
rubber waste	1	5

Thus, the investigated pyrolysis product from rubber waste is relatively safe for use as a sorption material.

CONCLUSIONS

They studied the solid pyrolysis product from carbonaceous wastes (used automobile tires) after the treatment with "dry" ashing as the sources of migration to the aqueous phase of harmful ingredients in the form of macro-ions.

They obtained the values of the observed specific electrical conductivity, NaCl mineralization, and the mass concentration of macro-cations (NH_4^+,Na^+,K^+,Mg^{2+},Ca^{2+}) and macro anions (F^-,Cl^-,NO_3^-,PO_4^{3-},SO_4^{2-}) in the water extract of SPP CCW.

The macro ions that undergo the emissions into the aqueous phase are arranged in the following series in value decrease order:

SO_4^{2-}, Ca^{2+}, K^+, Na^+, Cl^-, Mg^{2+}, NH_4^+, NO^{3-}, F^-.

The content of harmful ingredients in the aqueous extract of a solid pyrolysis product from rubber waste after ashing was compared with the normative indices of the aquatic environment. The concentration factors were calculated with respect to the standards for drinking water, fishery water, the sewage for discharge to a centralized system.

The obtained results show that the water extract of the TPP after the treatment with "dry" ashing does not exceed the normative indices for sewage by the content of macro-ions.

The toxicity of SPP CCW after ashing was determined experimentally on the mortality of the Daphnia magna Straus test object. According to the criteria for hazardous waste classification as a hazard class for the environment [11], the SPP of rubber waste under study belongs to the fifth hazard class.

SUMMARY

It has been established that the solid pyrolysis product from rubber waste after the treatment with "dry" ashing does not make a negative impact on water bodies, which justifies the possibility of test sample use from environmental positions as a potential sorption material.

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